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This report is one of a series which assesses the potential air pollution impacts of 14 industrial chemicals outside the work environment. Topics covered in each assessment include physical and chemical properties, health and welfare effects, ambient concentrations and measurement methods, emission sources, and emission controls. The chemicals investigated in this report series are:

Volume I	Acetylene	Volume VIII	Formaldehyde
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Volume III	Ethylene Dichloride	Volume X	Ortho-Xylene
Volume IV	Benzene	Volume XI	Maleic Anhydride
Volume V	Acetone	Volume XII	Dimethyl Terephthalate
Volume VI	Acrylonitrile	Volume XIII	Adipic Acid
Volume VII	Cyclohexanone	Volume XIV	Phthalic Annydride

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ASSESSMENT OF METHYL ALCOHOL AS A POTENTIAL AIR POLLUTION PROBLEM

Volume II

by

Robert M. Patterson
Mark I. Bornstein
Eric Gorshick

GCA CORPORATION
GCA/TECHNOLOGY DIVISION
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EPA Project Officer

Michael Jones

EPA Task Officer

Justice Manning

U.S. ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park
North Carolina 27711

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Volume IX	Methyl Methacryiate
Volume X	Ortho-Xylene
Volume XI	Maleic Anhydride
Volume XII	Dimethyl Terephthalate
Volume XIII	Adipic Acid
Volume XIV	Phthalic Anhydride.

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SECTION I

SUMMARY AND CONCLUSIONS

Methyl alcohol is a clear, colorless, flammable liquid. Traditionally it has been manufactured by the destructive distillation of wood. Modern manufacture is based on the catalytic reduction of carbon monoxide or carbon dioxide with hydrogen. Some main uses of methyl alcohol are as a solvent, an antifreeze, and as a starting material for formaldehyde and other chemicals.

Methyl alcohol poisoning occurs through inhalation of the vapor, although cases of poisoning through ingestion are not uncommon. Vapor concentrations above 30,000 ppm at exposure times exceeding 30 to 60 minutes are dangerous to man and may produce acute poisoning. Acute poisoning occurs indirectly by metabolic oxidation of methyl alcohol in the body to poisonous chemicals such as formaldehyde and formic acid. The current OSHA standard for workers is a time weighted average of 200 ppm for an 8-hour day. The photochemical reactivity of methyl alcohol is not significant.

Methyl alcohol emissions are estimated to be 1,242 million pounds/year, with solvent usage producing almost 90 percent of the total. Methyl alcohol is used as a solvent in many products including inks, dyes, waterproofing formulations and windshield cleaners. In addition, it is used throughout the chemical industry in extracting, washing, and crystallizing operations. Therefore, methyl alcohol emissions are produced by many small, geographically scattered sources. Methyl alcohol is produced at 12 locations, primarily in Texas and Louisiana, but only 5 percent of the total emissions are associated with the production process. Production is

estimated to have been 6,789 million pounds in 1974, and it is expected to increase by 8 percent per year through 1978.

The literature does not report specific control equipment for methyl alcohol emissions, but control devices for other similar hydrocarbons are reported. Two types of control devices presently used extensively by the industry to control hydrocarbon emissions are vapor recovery and incineration. Both systems have reported efficiencies of 95 percent and higher. Vapor recovery by adsorption on activated charcoal is usually used at inlet concentrations above 2,500 ppm when recovery is economically desirable. Incineration by direct oxidation and catalytic oxidation are also used. Catalytic oxidation is used at low methyl alcohol concentrations to minimize the amount of supplemental fuel required.

Simple diffusion model calculations place the expected maximum 1-hour and 24-hour average ambient concentrations near production facilities at 25 ppm and 14 ppm, respectively.

Based on available health effects studies and expected maximum ambient concentrations presented in this report, it appears that methyl alcohol in air does not pose a health hazard to the general population nor does it pose other environmental hazards. It is, however, possible that consumer misuse of methyl alcohol, such as use in confined spaces, could cause untoward health effects on an individual basis.

SECTION II

AIR POLLUTION ASSESSMENT REPORT

PHYSICAL AND CHEMICAL PROPERTIES

Methyl alcohol is a clear, colorless, flammable liquid. Traditionally it has been manufactured by the destructive distillation of wood. Modern manufacture is based on the catalytic reduction of carbon monoxide or carbon dioxide with hydrogen. Some main uses of methyl alcohol are as a solvent, an antifreeze, and as a starting material for formaldehyde and other chemicals.[1] Selected physical and chemical properties are presented in Table 1.

Table 1. SIGNIFICANT PROPERTIES OF METHYL ALCOHOL

Synonyms: methanol, carbinol, Columbian spirit, wood alcohol, wood spirit	
Chemical formula	CH_3OH
Molecular weight	32.042
Boiling point	64.5°C
Melting point	-97.8°C
Specific gravity	0.792 (20°/4°C)
Vapor density	1.11 (air = 1)
Vapor pressure	92 mm Hg at 20°C
Solubility	Soluble in water, alcohols, ketones, esters, and halogenated hydrocarbons
Explosive limits	6.0 to 36.5 percent by volume
Auto ignition temperature	470°C
Flash point	12°C (closed cup)
At 25°C and 760 mm Hg	1 ppm vapor = 1.309 mg/m^3 1 mg/m^3 vapor = 0.764 ppm

HEALTH AND WELFARE EFFECTS

Effects on Man

Acute Poisoning - Acute exposure of man to methyl alcohol vapor has not been well documented. There are early unquantified reports[2,3] on workers who suffered dizziness, nausea and various degrees of blindness when exposed to methyl alcohol-based solvent fumes for several hours. Methyl alcohol can induce a mild stupor in man, but its initial effect upon the central nervous system is greater in animals.[4] Its primary toxicity in man is due to its metabolic oxidation products, formaldehyde and formic acid. Acute poisoning causes severe acid imbalance with symptoms including headache, nausea, and vomiting and eventually leading to delirium, coma, respiratory collapse, and death. Optic nerve and retinal destruction leading to blindness may accompany acidosis. However, a single brief exposure to the vapor at a high concentration usually only causes temporary blindness, mucous membrane irritation, and slight intoxication, with recovery dependent on individual susceptibility and duration of exposure. A concentration of 2000 ppm is barely detectable by odor and not irritating to man, and only at 50,000 ppm does exposure become unendurable.[5] Cases of death include a woman exposed to a calculated 4,000 - 13,000 ppm for 12 hours[6] and a man exposed to 40,000 ppm for part of a working day.[7] The symptoms of poisoning are delayed 6 to 36 hours due to the slow accumulation of toxic metabolic products. Based primarily on extrapolation of animal inhalation studies to man, it would be dangerous for a man to be exposed to 30,000 - 50,000 ppm for 30 to 60 minutes.[5]

The liquid and vapor will cause skin irritation and can be absorbed through the skin, with poisoning possible but not likely. Using data obtained with monkeys, it was estimated that 1 ounce of methyl alcohol must be absorbed through the skin to affect man.[3] The usual route of acute poisoning is ingestion when methyl alcohol has been mistaken for ethyl alcohol.[8] Death has resulted from ingestion of 340 mg/kg body

weight.[9] Methods of treatment for ingestion include the administration of ethyl alcohol which inhibits methyl alcohol oxidation, the administration of alkali to combat the acidosis, and hemodialysis[10] or filtration of the blood.

Chronic Poisoning - Table 2 summarizes available dose-response data for chronic exposure to methyl alcohol vapor. Early unquantified reports have indicated chronic exposure could lead to complete blindness, in addition to headache, mucous membrane irritation, and neuritis. Workers who were working with a methyl alcohol-based ink in an enclosed area were exposed to concentrations in the 300 - 800 ppm range and complained of headaches.[4] On the basis of human exposure, it was calculated that repeated 8-hour exposures to 1,000 ppm will lead to increasing methyl alcohol concentrations inside the body that could cause an accumulation of toxic metabolic products. However, severe injury due to chronic exposure has not been a problem in recent years. On the basis of both human and animal exposure, the NIOSH recommended 8-hour time weighted average is 200 ppm.

Table 2. CHRONIC EXPOSURE OF MAN TO METHYL ALCOHOL VAPOR

Concentration, ppm	Exposure	Response	Reference
25	Daily workday	No effect	5
300	Daily workday	Headache	4
400-500	Daily average workday	No effect	5
800	Daily workday	Headache	4
1,000-2,000	Less than 30 minutes daily	No effect	7

Effects on Animals

Acute Poisoning - Animal response to inhalation of methyl alcohol in air varies with the species. Responses of different animals to lethal and

intermediate concentrations are presented in Table 3.[5] Exposure to acute concentration will generally induce the following responses in animals: increased rate of respiration, a state of nervous depression followed by excitation, irritation of the mucous membranes, ataxia (lack of muscular coordination), partial paralysis, narcosis (stupor or unconsciousness), convulsions, loss in weight, and death due to respiratory failure. The distribution of methyl alcohol in the tissues of dogs was associated with water content, with most of the methyl alcohol found in the blood, bile, and urine. Death in nonprimates is not due to acid imbalance induced by poisonous metabolic products, but rather to the narcotic action exerted on the central nervous system.[4,11] Autopsies have revealed considerable central nervous system degeneration. While some investigators have found optic degeneration in animals, blindness as found after human exposure is unusual.[5] As in man, poisoning through skin absorption is possible but not likely.

Table 3. ACUTE RESPONSE OF ANIMALS TO METHYL ALCOHOL VAPOR

Animal	Concentration, ppm	Exposure, hours	Response	Outcome
Cat	132,000	5-5.5	Narcosis	Died
	65,700	4.5	On side	50% died
	18,300	6	None	
Mouse	72,600	54	Narcosis	Death
	48,000	24	Narcosis	Survived
	10,000	230	Ataxia	Survived
Rat	60,000	7.5	Narcosis convulsions	Died
	50,000	1	Drowsiness	Survived
	27,500	8	Narcosis	
	8,800	8	Lethargy	
	4,800	8	None	
	3,000	8	None	
Dog	13,700	4	None	
	2,000	24	None	
Monkey	40,000	4	Illness	Death
	10,000	18 daily		Death
	1,000	41		Death

Chronic Poisoning - The few studies investigating animal chronic exposure to methyl alcohol vapor indicate no effect except at high levels for most animals. Dogs were exposed to 450 to 500 ppm for 8 hours daily for 379 days, and no ill effects such as unusual behavior, loss of weight, or eye abnormalities were seen. Two dogs exposed to 10,000 ppm for 3 minutes in 8 periods per day at hourly intervals for 100 consecutive days showed no symptoms of poisoning.[5] However, monkeys, rabbits, and rats exposed to 10,000 ppm for 7 hours per day for several weeks died. The lowest fatal concentration was for monkeys, some of which died after a few 18-hour exposures to 1,000 ppm.[3] Susceptibility among animals has been found to vary considerably even among individuals of the same species.

Effects on Vegetation

Methyl alcohol has not been implicated in vegetation damage as other pollutants, such as ethylene, nitrogen oxides, sulfur dioxide, and ozone, have. However, a recent Russian study has indicated that plants may be sensitive to methyl alcohol vapor in concentrations above 0.15 ppm.[12] Branches from eight different tree species were studied. The permissible pollutant standard (0.15 ppm) was taken as the concentration which did not produce a decrease in photosynthesis for 5 minutes. The significance of this study is the finding that plants are more sensitive to lower concentrations of the vapors than are either man or animals.

Other Effects

Effects on Materials - Methyl alcohol as a solvent will attack some forms of plastics, rubbers, and coatings. It may also react with metallic aluminum at high temperatures.[6]

Effects on Photochemical Smog - Methyl alcohol is not a significant component of photochemical smog. Furthermore, compared to the aromatics,

aliphatics, aldehydes and ketones, the alcohols are the least active in the formation of photochemical products upon irradiation.[13]

AMBIENT CONCENTRATIONS AND MEASUREMENT

Ambient Concentration Estimates

Although methyl alcohol emissions are greatest from the solvent usage source category, these sources tend to be small and geographically scattered. Production of methyl alcohol, however, occurs at a few locations for which the emissions characteristics can be fairly well defined, and which as single point or area sources have a large emission density.

The largest installation for methyl alcohol production is located near a city of about 100,000 population, and it has a capacity of about 1,500 million pounds per year. Assuming a 1 percent loss, this converts to an emission rate of:

$$\frac{(0.01 \text{ emission factor})\ (1{,}500 \times 10^{6} \text{ lb/yr})\ (453.6 \text{ g/lb})}{3.1536 \times 10^{7} \text{ sec/yr}}$$

$$= 215.8 \text{ g/sec of methyl alcohol.}$$

Some assumptions must be made regarding this methyl alcohol release to the atmosphere. First of all, the emissions do not all come from one source location, but rather from a number of locations where methyl alcohol vapor leaks to the atmosphere. Thus, the emissions can be characterized as coming from an area source which will be taken to be 100 meters on a side. Secondly, the emissions occur at different heights, and an average emission height of 10 meters is assumed.

Ground level concentrations can then be estimated at locations downwind of the facility.[14] To do this, a virtual point source of emission is assumed upwind of the facility at a distance where the initial horizontal dispersion coefficient equals the length of a side of the area divided by 4.3. In this case:

$$\sigma_{yo} = 100 \text{ m}/4.3 = 23.3 \text{ m}.$$

Assuming neutral stability conditions (Pasquill-Gifford Stability Class D) with overcast skies and light winds, the upwind distance of the virtual point source is approximately 310 meters. With consideration of the plant boundary, it is reasonable to assume that the nearest receptor location is thus about 500 meters from the virtual point source. Finally, taking 2 m/sec as an average wind speed, the ground level concentration may be calculated from

$$\chi = \frac{Q}{u\pi\sigma_y\sigma_z} e^{-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2}$$

or

$$\chi = \frac{215.8}{(2)\pi(36)(18.5)} e^{-\frac{1}{2}\left(\frac{10}{18.5}\right)^2}$$

$$= 4.456 \times 10^{-2} \text{ g/m}^3$$

for a 10-minute average concentration. Over a period of an hour this becomes $(4.456 \times 10^{-2} \text{ g/m}^3)$ $(0.72) = 3.208 \times 10^{-2}$ g/m^3 or 25 ppm 1-hour average concentration. Over a 24-hour period, the average concentration might roughly be expected to be about 14 ppm.

Measurement Technology

Two sample collection techniques are used in air sampling for methyl alcohol. These are collection in distilled water in a bubbler or impinger,[15] and collection on silica gel.[16] Analysis of samples collected by the first technique is achieved by colorimetric methods, whereas gas chromatography is used to analyze samples collected on silica gel.

Using the bubbler or impinger collection method, concentrations as low as 10 ppm may be determined. The colorimetric determination is based on the development of formaldehyde through oxidation of the methyl alcohol with potassium permanganate. Thus, formaldehyde, or chemicals which will form formaldehyde by oxidation by potassium permanganate, will interfere with the determination.

The gas chromatographic technique has the advantage of not requiring the handling of chemicals in the field, and is by far the more sensitive ($\simeq$0.01 ppm) of the two methods. Excess moisture in the air may prevent efficient adsorption of methyl alcohol on the silica gel.

SOURCES OF METHYL ALCOHOL EMISSIONS

The production of methyl alcohol is estimated to have been 6,789 million pounds in 1974 and is expected to increase at 8 percent per year through 1978.[17] Methyl alcohol is primarily used to manufacture formaldehyde, accounting for 39 percent of the methyl alcohol consumed. Methyl alcohol is also used extensively in industry as a solvent and by the consumer in cleaning agents. This second usage accounts for approximately 16 percent of all methyl alcohol consumed. The consumption of methyl alcohol for final products is shown in Table 4. This table also shows the expected growth rate for each sector.

Table 4. METHYL ALCOHOL CONSUMPTION - 1974[18]

Product	Millions of pounds	Annual % growth
Formaldehyde	2,646	7.4
Exports	785	Variable
Industrial solvent usage	538	8.0
Dimethyl terephthalate	414	15.7
Methyl methacrylate	252	8.5
Acetic acid	229	17.0
Methylamines	221	8.5
Glycol methyl ethers	77	2.5
Inhibitor for formaldehyde	63	4.0
Miscellaneous (50 percent miscellaneous solvent)	1,150	Expected to increase Unknown rate
Total	6,789	8.0

Methyl Alcohol Sources and Emission Estimates

Emissions of methyl alcohol occur from miscellaneous solvent usage, industrial solvent usage, methyl alcohol production, end product manufacturing and bulk storage and handling losses. Total emissions of methyl alcohol are estimated to have been 1,242 million pounds in 1974 representing 18 percent of total production (see Table 5).

The largest source of emissions is the miscellaneous solvent usage category. Methyl alcohol is used directly as a solvent for inks, dyes, certain resins and cements, the manufacture of wood and metal surface coatings, waterproofing formulations, coated fabrics, and windshield cleaner and deicer. All methyl alcohol used for these categories is assumed to be lost in the atmosphere, resulting in emissions of 575 million pounds/year.[17,18]

Table 5. METHYL ALCOHOL SOURCES AND EMISSION ESTIMATES

Source	Emissions, million pounds/year
Miscellaneous solvent usage	575
Industrial solvent usage	538
Methyl alcohol production	68
End product manufacturing	49
Storage and handling	12
Total	1,242

The next major source of emissions is industrial solvent usage. Methyl alcohol is used extensively in the chemical industry as a solvent for extracting, washing, drying, and crystallizing. It is also used in refining gasoline and heating oil to extract mercaptan impurities. Emissions from industrial solvent usage are estimated to be 538 million pounds based on 100 percent loss of solvent.

Emission factors for methyl alcohol losses from production and final product manufacturing are both estimated to be 0.01 pound of methyl alcohol lost per pound of methyl alcohol produced or used (1 percent loss). This figure is based upon the reported loss of methyl alcohol from manufacturing formaldehyde, the major use of methyl alcohol.[19] The assumption was also made that losses from the production of methyl alcohol (10 companies, 12 locations - see Table 6) would be similar to losses from the manufacture of final products. Using this factor, emissions from production losses are 68 million pounds and losses from the manufacture of final products are 49 million pounds.

The last major source is from bulk storage and handling. Using the factors available from AP-42[20] and assuming all tanks have fixed roofs, emissions are 12 million pounds per year.

Table 6. METHYL ALCOHOL PRODUCERS - 1974

Company	Location	Capacity, million lb/yr
Air Products	Pensacola, Fla.	332
Borden	Geismar, La.	1,061
Celanese	Bishop, Texas	398
Celanese	Clear Lake, Texas	1,525
CSC	Sterlington, La.	332
Dupont	Beaumont, Texas	1,326
Dupont	Orange, Texas	762
Georgia Pacific	Plaquemine, La.	663
Hercules	Plaquemine, La.	663
Monsanto	Texas City, Texas	663
Rohm and Haas	Deer Park, Texas	146
Tenneco	Houston, Texas	530
Total		8,401

METHYL ALCOHOL EMISSION CONTROL METHODS

The literature does not report specific control equipment for methyl alcohol emissions, but it does report control devices for other similar hydrocarbons. Two types of control devices are presently used extensively by the industry to control hydrocarbon emissions, vapor recovery and incineration. Both systems have reported efficiencies of 94 percent and higher.

Adsorption

Control of hydrocarbon emissions by adsorption on activated charcoal is generally applied when recovery of adsorbed material is economically desirable. Adsorption should be used when concentrations of hydrocarbons are greater than 2,500 ppm.[21] Other applications are for the

control of very low concentration hydrocarbons that are poisonous to catalytic incinerators and for collection and concentration of emissions for subsequent disposal by incineration. Cost data for the cases utilizing adsorption are presented in Tables 7 and 8. The three cases presented are adsorption with solvent recovery, adsorption with incineration, and adsorption with incineration plus heat recovery.

Table 7. ESTIMATED INSTALLED COSTS OF ADSORPTION SYSTEMS[a]

Adsorber capacity, SCFM	1,000	10,000	20,000
With solvent recovery, $	74,000	162,300	280,000
With thermal incineration/ no heat recovery, $	89,500	202,000	344,000
With thermal incineration/ primary heat recovery, $	101,500	255,000	431,000

[a]Reference 22. Inlet concentration assumed to be 25 percent of lower explosive limit. Costs updated to first quarter 1975.

Table 8. ESTIMATED ANNUAL OPERATING COSTS OF ADSORPTION SYSTEMS[a]

Adsorber capacity, SCFM	1,000	10,000	20,000
With solvent recovery, $/yr	13,200	-10,479[b]	-37,200[b]
With thermal incineration/ no heat recovery, $/yr	23,400	64,300	123,200
With thermal incineration/ primary heat recovery, $/yr	25,600	82,000	141,600

[a]Reference 22. Inlet concentration assumed to be 25 percent of lower explosive limit. Costs updated to first quarter 1975.

[b]Indicates a savings as opposed to operating cost.

Incineration

Control of methyl alcohol emissions by incineration or catalytic oxidation involves oxidation of the combustible portion of the effluent, the desired ultimate products being water and carbon dioxide.

The primary advantage of catalytic incineration is that extremely small concentrations of organics can be oxidized with only small amounts of supplemental fuel required. The main disadvantages are the higher capital cost and the fact that certain hydrocarbons may poison the catalyst. Cost data for thermal and catalytic incinerators with and without heat recovery are presented in Tables 9 and 10.[22]

Table 9. ESTIMATED INSTALLED COSTS OF THERMAL AND CATALYTIC INCINERATORS[a]

Incinerator capacity, SCFM	1,000	10,000	20,000
Installed costs, $			
Catalytic without heat recovery	43,500	272,000	504,600
Catalytic with primary heat recovery	54,100	306,000	573,900
Catalytic with primary and secondary heat recovery	68,300	361,800	666,400
Thermal without heat recovery	27,200	92,500	137,400
Thermal with primary heat recovery	40,300	144,200	232,600
Thermal with primary and secondary heat recovery	54,400	200,000	322,300

[a]Reference 22. Inlet concentration assumed to be 25 percent of lower explosive limit. Costs updated to first quarter 1975.

Table 10. ESTIMATED ANNUAL OPERATING COSTS OF THERMAL AND CATALYTIC INCINERATORS[a]

Incinerator capacity, SCFM - based on 25% lower explosive limit	1,000	10,000	20,000
Operating costs, $/yr			
Catalytic without heat recovery	16,200	102,800	195,000
Catalytic with primary heat recovery	16,400	78,500	177,900
Catalytic with primary and secondary heat recovery	19,300	108,700	203,700
Thermal without heat recovery	12,000	54,300	96,700
Thermal with primary heat recovery	11,500	36,300	59,200
Thermal with primary and secondary heat recovery	14,400	50,800	84,500

[a]Reference 22. Inlet concentration assumed to be 25 percent of lower explosive limit. Costs updated to first quarter 1975.

Storage Tanks

Control of emissions from storage tanks will require the use of floating roof tanks or venting the emissions to the previously mentioned adsorber or incinerator. Emissions from fixed roof tanks can be vented to either system without any major increase in cost. If these systems are not available the fixed roof tanks should be converted to floating roof tanks, resulting in a 90 percent reduction of emissions. Figure 1 provides estimated costs of various gasoline storage tanks.[22] These equipment cost estimates can also be applied to methyl alcohol. As can be seen, conversion of fixed roof to floating roof tanks by installation of internal floating covers is much more economical than installation of new pontoon floating tanks.

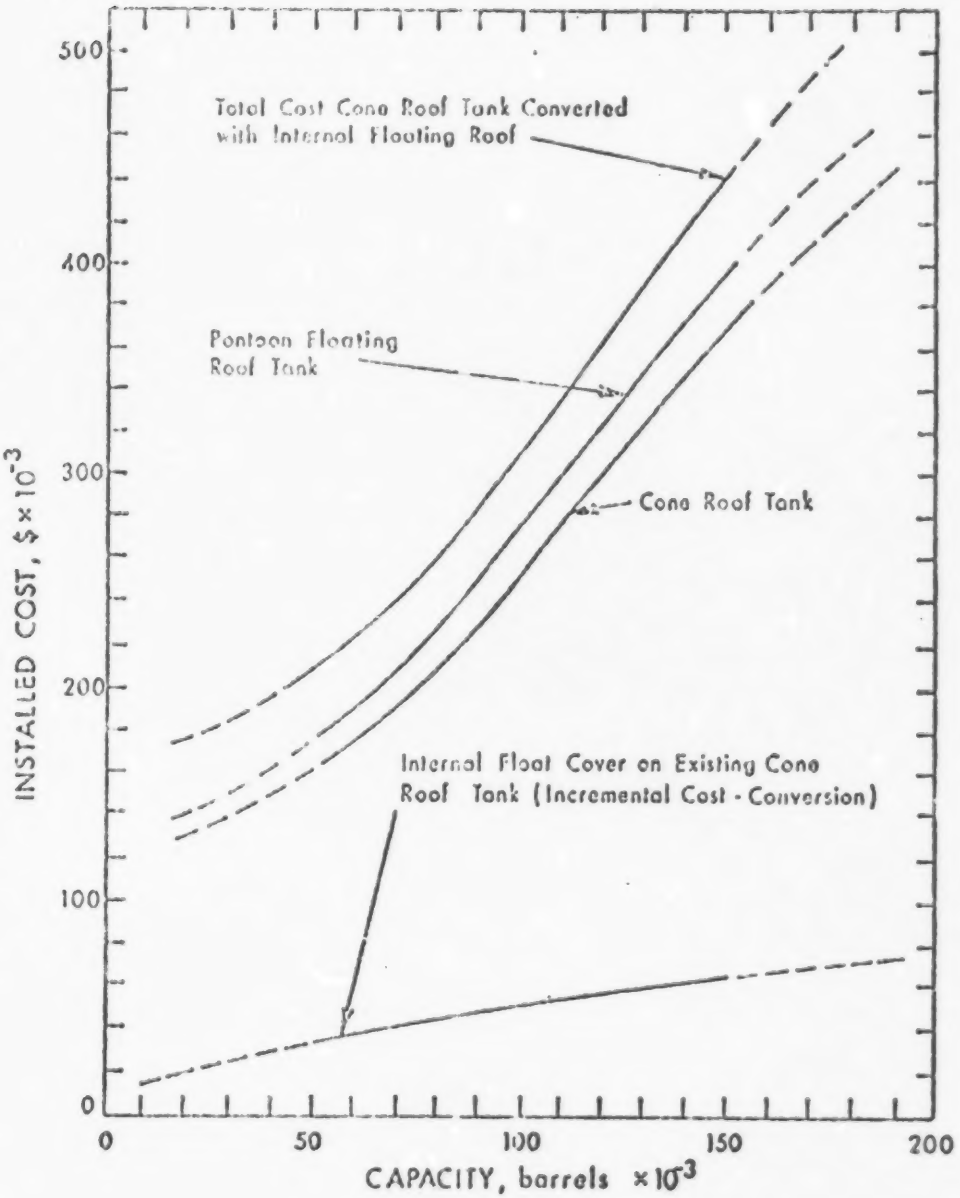

Figure 1. Estimated installed cost of methyl alcohol storage tanks (equipment costs assumed to be the same as gasoline storage tanks)[22]

SECTION III

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